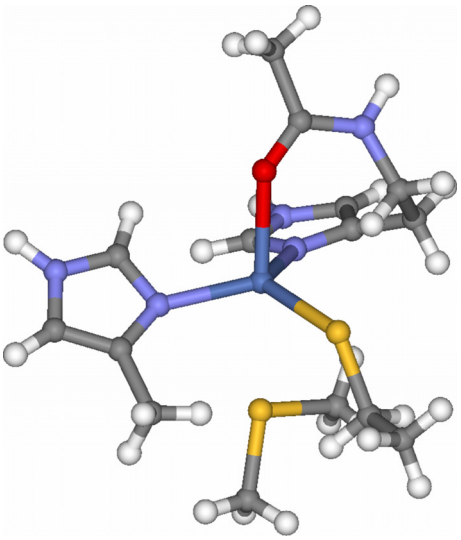
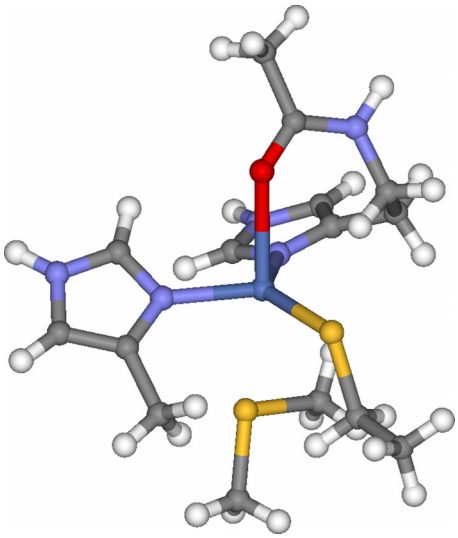
**S1.** Geometric Structure and ADF Input information for NiAz S1-B used for calculations shown in the main manuscript.



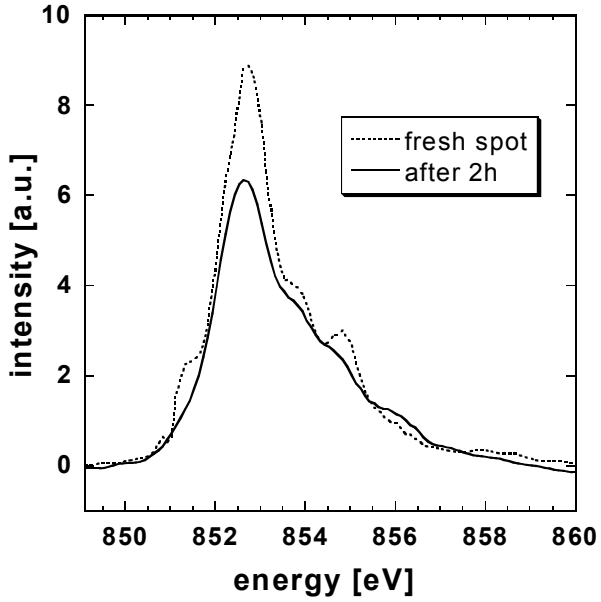
```
(INPUT FILE)
scf
  converge    0.00000001
  mixing      0.15
  iterations  200
end
xc
   lda vwn
   gga pw91
end
integration 7.0
symmetry  NOSYM
charge +1.00 2.00
unrestricted
Atoms  Cartesian
 Ni   0.0000   0.0000   0.0000
 S   -0.2200   3.1460 -1.0030 f=Met
 C    0.4940   4.7850 -0.8420 f=Met
 C   -1.9320   3.5990 -0.8250 f=Met
 H    1.4891   4.7247 -0.9193 f=Met
 H    0.2521   5.1684  0.0494 f=Met
 H    0.1391   5.3763 -1.5662 f=Met
 H   -2.5025   2.7803 -0.8905 f=Met
 H   -2.1849   4.2397 -1.5500 f=Met
 H   -2.0719   4.0318  0.0656 f=Met
 S   -0.0640   0.5470  2.3620 f=Cys
 C    0.1760   2.2850  4.4460 f=Cys
 C   -0.1170   2.2400  2.9640 f=Cys
 H    0.1426   3.2324  4.7642 f=Cys
 H    1.0862   1.9080  4.6179 f=Cys
 H   -0.5066   1.7444  4.9378 f=Cys
 H   -1.0267   2.6201  2.7970 f=Cys
 H    0.5665   2.7837  2.4770 f=Cys
 C    3.2770   1.6440  0.2770 f=His
 C    3.0540   0.6080 -0.8240 f=His
 N    1.8650   0.1040 -0.9990 f=His
 C    3.9860   0.0660 -1.6550 f=His
 C    2.0310 -0.7790 -1.9550 f=His
 N    3.2930 -0.7940 -2.3420 f=His
 H    2.4055   1.8521  0.7210 f=His
 H    3.6550   2.4793 -0.1223 f=His
 H    3.9166   1.2794  0.9538 f=His
 H    1.3078 -1.3559 -2.3347 f=His
 H    4.9613   0.2767 -1.7209 f=His
 H    3.6633 -1.3825 -3.0607 f=His
 C   -1.4910 -4.3380 -0.6540 f=HisGly
 C   -1.5310 -2.9280 -0.0890 f=HisGly
 O   -0.5220 -2.1870 -0.1150 f=HisGly
 N   -2.7140 -2.4870  0.3470 f=HisGly
 C   -2.8940 -1.2200  1.0480 f=HisGly
 C   -3.6740 -0.1430  0.2930 f=HisGly
 C   -3.0620  0.2030 -1.0610 f=HisGly
 N   -1.7550  0.2300 -1.2550 f=HisGly
 C   -3.7710  0.2930 -2.2130 f=HisGly
 C   -1.6350  0.3330 -2.5650 f=HisGly
 N   -2.8360  0.3660 -3.1140 f=HisGly
 H   -3.5100 -3.0700  0.2310 f=HisGly
 H   -3.3802 -1.4086  1.9013 f=HisGly
 H   -1.9871 -0.8529  1.2547 f=HisGly
 H   -2.3867 -4.7681 -0.5417 f=HisGly
 H   -0.8012 -4.8734 -0.1666 f=HisGly
 H   -1.2587 -4.3016 -1.6260 f=HisGly
 H   -0.7698  0.3789 -3.0643 f=HisGly
 H   -4.7631  0.3012 -2.3384 f=HisGly
 H   -3.0047  0.4379 -4.0970 f=HisGly
 H   -4.6072 -0.4708  0.1456 f=HisGly
 H   -3.6957  0.6852  0.8530 f=HisGly
end
fragments
  Ni      ./Ni-p2-TZ2Ppw-ae.t21
  Met     ./S1B-Met.t21
  Cys     ./S1B-Cys.t21
  His     ./S1B-His.t21
  HisGly ./S1B-HisGly.t21
end
end input
```

**S2.** Alternative geometric structure of NiAz from S2-B with a longer Ni-O axial bond distance. All results from this calculation are given as Supporting Information.

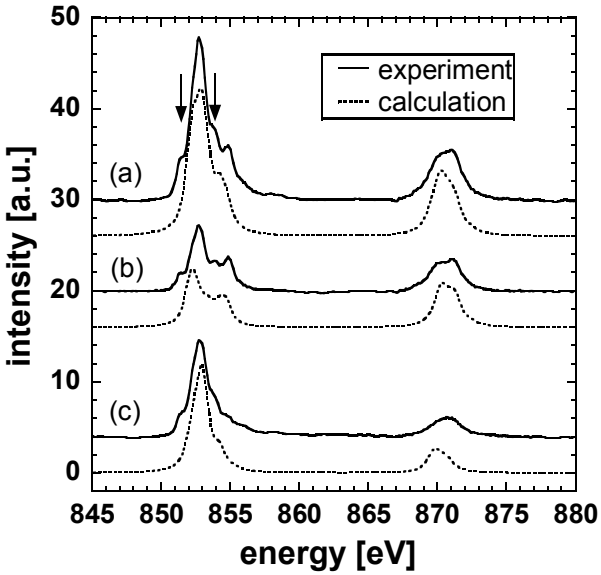


```
(INPUT FILE)
scf
  converge    0.00000001
  mixing      0.15
  iterations  200
end
xc
   lda vwn
   gga pw91
end
integration 7.0
symmetry  NOSYM
charge +1.00 2.00
unrestricted
modifystartpotential
  Ni  5 // 3
end
Atoms  Cartesian
 Ni  0.0000  0.0000  0.0000
 S  -0.1276  3.0430 -1.3877 f=Met
 C   0.4900  4.7118 -1.2022 f=Met
 C  -1.8481  3.4228 -1.2883 f=Met
 H   1.4894  4.7032 -1.2340 f=Met
 H   0.1881  5.0838 -0.3244 f=Met
 H   0.1383  5.2823 -1.9444 f=Met
 H  -2.3812  2.5813 -1.3750 f=Met
 H  -2.0946  4.0506 -2.0266 f=Met
 H  -2.0448  3.8521 -0.4068 f=Met
 S   0.0011  0.3979  2.2183 f=Cys
 C   0.0331  2.4247  4.1294 f=Cys
 C  -0.0615  2.1664  2.6099 f=Cys
 H  -0.0048  3.4086  4.3037 f=Cys
 H   0.8959  2.0580  4.4772 f=Cys
 H  -0.7307  1.9750  4.5926 f=Cys
 H  -0.9244  2.5418  2.2717 f=Cys
 H   0.7027  2.6250  2.1563 f=Cys
 C   3.0394  1.5994  0.2307 f=His
 C   2.9355  0.4226 -0.7415 f=His
 C   1.9950 -1.0050 -1.9566 f=His
 N   1.7847 -0.1939 -0.9360 f=His
 C   3.8925 -0.0062 -1.6247 f=His
 N   3.2463 -0.8836 -2.3572 f=His
 H   2.4283  2.3330 -0.0668 f=His
 H   3.9806  1.9365  0.2474 f=His
 H   2.7772  1.2989  1.1477 f=His
 H   1.3137 -1.6147 -2.3618 f=His
 H   4.8484  0.2792 -1.6941 f=His
 H   3.5794 -1.2498 -3.1920 f=His
 C  -1.2918 -4.5231 -0.6862 f=HisGly
 C  -1.4065 -3.1093 -0.1267 f=HisGly
 O  -0.4045 -2.3964 -0.0338 f=HisGly
 N  -2.5909 -2.6523  0.2578 f=HisGly
 C  -2.7551 -1.3341  0.8191 f=HisGly
 C  -3.5095 -0.3848 -0.1113 f=HisGly
 C  -2.8151 -0.0116 -1.4130 f=HisGly
 N  -1.5166  0.1680 -1.5183 f=HisGly
 C  -3.4412  0.0646 -2.6094 f=HisGly
 C  -1.3079  0.3527 -2.8071 f=HisGly
 N  -2.4592  0.2902 -3.4363 f=HisGly
 H  -3.3825 -3.2355  0.2059 f=HisGly
 H  -3.2641 -1.4131  1.6763 f=HisGly
 H  -1.8502 -0.9500  1.0024 f=HisGly
 H  -2.1937 -4.9549 -0.6898 f=HisGly
 H  -0.6689 -5.0584 -0.1156 f=HisGly
 H  -0.9375 -4.4847 -1.6205 f=HisGly
 H  -0.4188  0.5138 -3.2354 f=HisGly
 H  -4.4163 -0.0289 -2.8100 f=HisGly
 H  -2.5669  0.3234 -4.4028 f=HisGly
 H  -4.3801 -0.8176 -0.3451 f=HisGly
 H  -3.6821  0.4609  0.3937 f=HisGly
end
fragments
  Ni     ./Ni-p2-TZ2Ppw-ae.t21
  Met    ./S2B-Met.t21
  Cys    ./S2B-Cys.t21
  His    ./S2B-His.t21
  HisGly ./S2B-HisGly.t21
end
end input
```

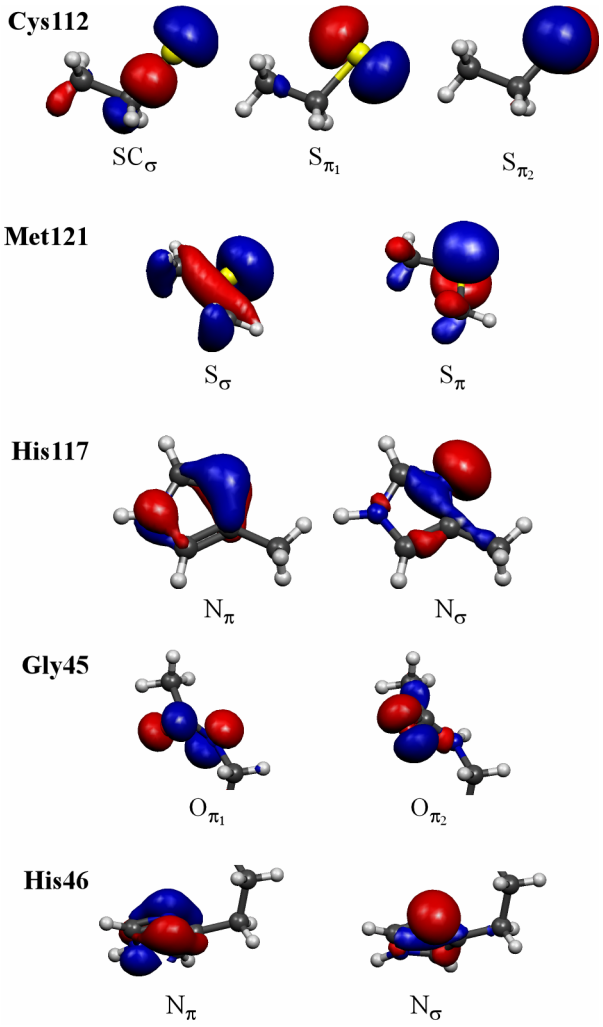
**S3.** Spectrum showing the effect of X-ray irradiation on the $L_3$ peak (solid line). The dotted line is the spectrum obtained from a fresh sample of NiAz.




**S5.** Calculated spectra for the crystal structure S2. L-edge XAS spectra of NiAz taken with left (b) and right (c) circularly polarized X-rays; spectrum (a) shows the sum of both contributions. Dotted lines are simulations; full lines are measured data.




**S4.** Important ligand fragment orbitals for Met121, Cys112, His117, His45, and Gly46. The labels used in Tables 2, 3 and S6 refer to those given in this figure.



**S6.** DFT results for structure S2. Results are presented in two tables that correlate directly with Tables 2 and 3 in the manuscript for structure S1.

| ***S2-B*** | Orbital | | Energy (eV) | Occ | Ni | | | Met121 | | Cys112 | | | His117 | | His46 | | Gly45 | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | 3d | 4s | 4p | $S_\sigma$ | $S_\pi$ | $SC_\sigma$ | $S_{\pi1}$ | $S_{\pi2}$ | $N_\pi$ | $N_\sigma$ | $N_\pi$ | $N_\sigma$ | $O_{\pi1}$ | $O_{\pi2}$ |
| Ni $3d_{x2-y2}$ | 111a | (β) | -6.077 | 0 | 0.1 | 1.2 | 56.5 | | 0.1 | 0.1 | 0.3 | 32.7 | | 4.7 | | 2.3 | | 0.1 |
| Ni $3d_{z2}$ | 110a | (β) | -6.692 | 0 | 4.5 | 0.4 | 71.9 | 0.6 | 5.9 | 0.1 | 9.4 | 0.4 | | 0.3 | | | 0.1 | 4.8 |
| Ni $3d_{xy}$ | 109a | (β) | -7.025 | 1 | 0.6 | 4.9 | 58.9 | 0.1 | | 0.1 | 23.0 | 4.4 | | 2.1 | | 1.1 | 0.4 | 0.6 |
| C112 $S_\sigma$ | 111a | (α) | -7.343 | 1 | | -0.1 | 18.5 | | | | | 73.1 | | 2.9 | | 1.7 | 0.1 | 0.1 |
| C112 $S_\pi$ | 110a | (α) | -7.488 | 1 | 2.8 | 6.4 | 31.3 | | 6.5 | 0.2 | 44.9 | 0.1 | 0.5 | 1.9 | | 0.5 | 0.2 | 0.7 |
| C112 $S_\pi$ | 108a | (β) | -7.640 | 1 | | 2.8 | 49.7 | | 1.1 | 0.7 | 0.9 | 36.2 | | 1.1 | | 1.5 | | 1.5 |
| M121 $S_\pi$ | 107a | (β) | -7.799 | 1 | 0.5 | 0.8 | 29.5 | 0.1 | 53.7 | 0.1 | 1.3 | 8.9 | | | | 0.8 | | 1.8 |
| M121 $S_\pi$ | 109a | (α) | -7.828 | 1 | 0.1 | 0.9 | 8.9 | | 84.2 | | 1.0 | | 0.1 | 0.9 | | 0.6 | 0.3 | 1.6 |
| Ni $3d_{xz}$ | 106a | (β) | -7.895 | 1 | 0.1 | 0.4 | 51.9 | 0.1 | 35.8 | 0.4 | 0.5 | 6.2 | | | | 0.1 | | 0.6 |
| Ni $3d_{yz}$ | 105a | (β) | -8.127 | 1 | | 0.3 | 78.1 | 0.1 | 0.1 | 5.3 | 2.2 | 4.1 | | 0.1 | | 0.2 | 1.1 | 0.6 |
| Ni 3d | 107a | (α) | -8.413 | 1 | 0.4 | 0.9 | 59.5 | 0.4 | 1.7 | 0.5 | 0.6 | 1.2 | 1.5 | | | 0.3 | 0.1 | 25.5 |
| Ni 3d | 106a | (α) | -8.619 | 1 | 1.2 | 2.2 | 63.0 | 1.2 | 2.2 | 4.3 | 6.8 | 2.9 | 0.1 | 5.7 | | 1.5 | | 6.2 |
| C112 $S_\sigma$ | 103a | (β) | -8.696 | 1 | 1.8 | 0.8 | 32.2 | 0.1 | | 6.2 | 31.7 | | | | | 0.4 | 4.8 | 15.8 |
| Ni 3d | 105a | (α) | -8.752 | 1 | 0.3 | 0.5 | 68.1 | 0.2 | 0.4 | 4.1 | | 0.4 | 3.2 | | | | 6.7 | 13.2 |
| Ni 3d | 103a | (α) | -8.918 | 1 | 0.1 | 3.8 | 56.1 | 0.2 | 0.1 | 0.5 | 0.7 | 13.4 | 0.9 | 4.6 | | 8.2 | 5.4 | 2.3 |

| Fragment | Mulliken | | | Hirshfeld | | | Multipole-Derived | | |
|---|---|---|---|---|---|---|---|---|---|
| | *q* | *s* | $k_{avg}(s)$ | *q* | *s* | $k_{avg}(q)$ | *q* | *s* | $k_{avg}(q)$ |
| Ni | 0.293 | 1.390 | 0.695 | 1.497 | - | 0.749 | 0.525 | 1.364 | 0.682 |
| Met121 | 0.139 | 0.060 | 0.030 | 0.063 | - | 0.032 | 0.108 | 0.063 | 0.031 |
| Cys112 | -0.028 | 0.436 | 0.218 | -0.632 | - | 0.184 | -0.131 | 0.443 | 0.221 |
| His117 | 0.242 | 0.045 | 0.022 | 0.021 | - | 0.010 | 0.187 | 0.056 | 0.028 |
| His46 | 0.190 | 0.045 | 0.023 | 0.051 | - | 0.025 | 0.150 | 0.049 | 0.025 |
| Gly45 | 0.163 | 0.025 | 0.012 | | | | 0.160 | 0.026 | 0.013 |

**S7.** $3d_\beta$ orbital splitting diagram obtained from DFT calculations on S2 and pattern used for multiplet simulations.